

Fragmentation patterns in the electron impact mass spectra of 1,3,5-triazin-2-one derivatives

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Abstract

Fragmentation patterns in the electron impact (EI) mass spectra of a series of 5-substituted 1,3,5-triazin-2-ones, prepared from the reaction of dimethylolurea with selected primary amines, have been elucidated using a combination of high-resolution, comparative low-resolution and metastable peak analysis. In addition to characteristic fragmentations, in which the triazine nucleus remains intact, the 5-substituted 1,3,5-triazin-2-ones appear to exhibit a series of extrusion/ring-contraction processes, resulting in the formation of 3- and 4-membered ring fragments. Resonance-stabilised even-electron ions, arising, in each case, from loss of a hydrogen atom from the molecular ion, are considered pivotal in the formation of these heterocyclic fragments.

Keywords: Triazinone, mass spectrometry, fragmentation patterns

Introduction

The emission of formaldehyde from urea-formaldehyde (UF) resins¹ may be reduced by decreasing the formaldehyde content² and adding cross-linking agents such as ammonia or melamine during the resinification process. The inclusion of ammonia has been found to result in the formation of triazine-urea-formaldehyde resins, the presence of three reactive sites in the triazine nucleus permitting cross-linking.³ While the mass spectra of 1,3,5-triazines have been

investigated,⁴ to our knowledge, no such studies of 1,3,5-triazin-2-ones have been reported. As part of a study of UF resins,⁵ we have prepared a series of 5-substituted 1,3,5-triazin-2-ones and, here, we discuss the electron impact (EI) mass spectra of the latter systems.

Results and Discussion

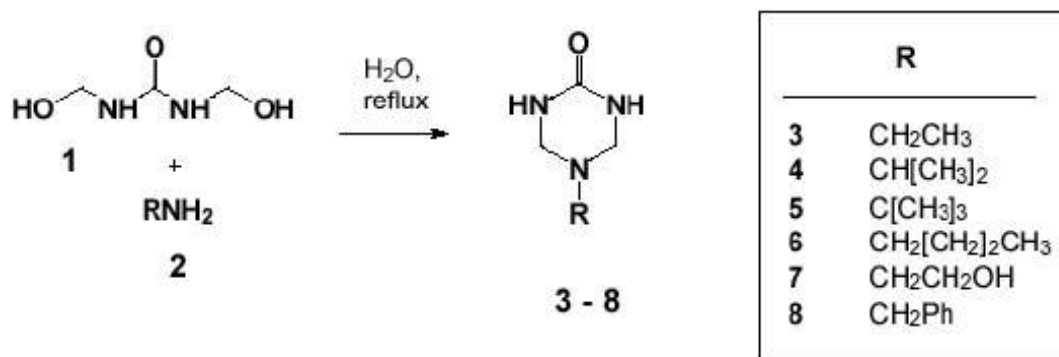
The triazinones **3-8** were prepared, following Burke's method,⁶ from dimethylolurea **1** and the corresponding primary amines **2** (Scheme 1). A combination of high-resolution, comparative low-resolution and metastable peak data was used to explore the fragmentation of these compounds. Selected MS data are summarised in Table 1 and the proposed fragmentation pathways are outlined in Schemes 2 and 3.

Table 1. Selected peaks (m/z ; followed, in parentheses, by % relative abundance) from EI mass spectra of 1,3,5-triazin-2-ones **3-8**, classified according to ion types A-I (Scheme 2)

Compd	R ¹	R ²	R ³	A	B	C	D	E	F	G	H	I
3	Me	H	H	129 ^a (23.1)	128 ^a (100.0)	114 ^a (5.2)	100 ^b (2.4)	- ^c	83 ^b (5.5)	99 ^a (15.8)	85 ^a (21.9)	56 ^a (7.6)
4	Me	H	Me	143 ^a (13.0)d	142 ^b (28.7)	128 ^a (100)d	100 ^b (2.6)	85 ^b (9.9)	83 ^b (3.6)	113 ^b (10.6)	99 ^a (24.2)d	56 ^b (62.8)
5	Me	Me	Me	157 ^a (8.7)	156 ^a (5.5)	142 ^a (88.2)	100 ^a (13.0)	85 ^a (3.3)	83 ^b (2.5)	127 ^b (0.5)	113 ^b (17.3)	56 ^a (6.7)
6	Pr	H	H	157 ^a (39.8)	156 ^a (60.7)	114 ^a (100)	100 ^a (4.5)	85 ^a (63.9)	83 ^b (2.8)	127 ^a (17.1)	113 ^a (19.0)	56 ^a (15.2)
7	CH ₂ OH	H	H	145 ^a (3.6)d	144 ^a (23.1)d	114 ^a (100)d	100 ^b (2.4)	85 ^a (86.6)d	83 ^b (5.4)	115 ^b (64.0)	101 ^b (13.0)	56 ^b (64.8)
8	Ph	H	H	191 ^a (2.4)	190 ^a (12.5)	190 ^a (0.9)	100 ^a (45.4)	85 ^a (1.3)	83 ^b (5.8)	161 ^a (1.5)	147 ^a (4.4)	56 ^a (2.6)

^a Atomic composition of fragment confirmed by high resolution analysis; % relative abundance from high-resolution spectrum. ^b Low-resolution MS data. ^c In this case, ion **E** has same nominal mass (m/z 85) as fragment **H**. ^d % Relative abundance from low-resolution spectrum.

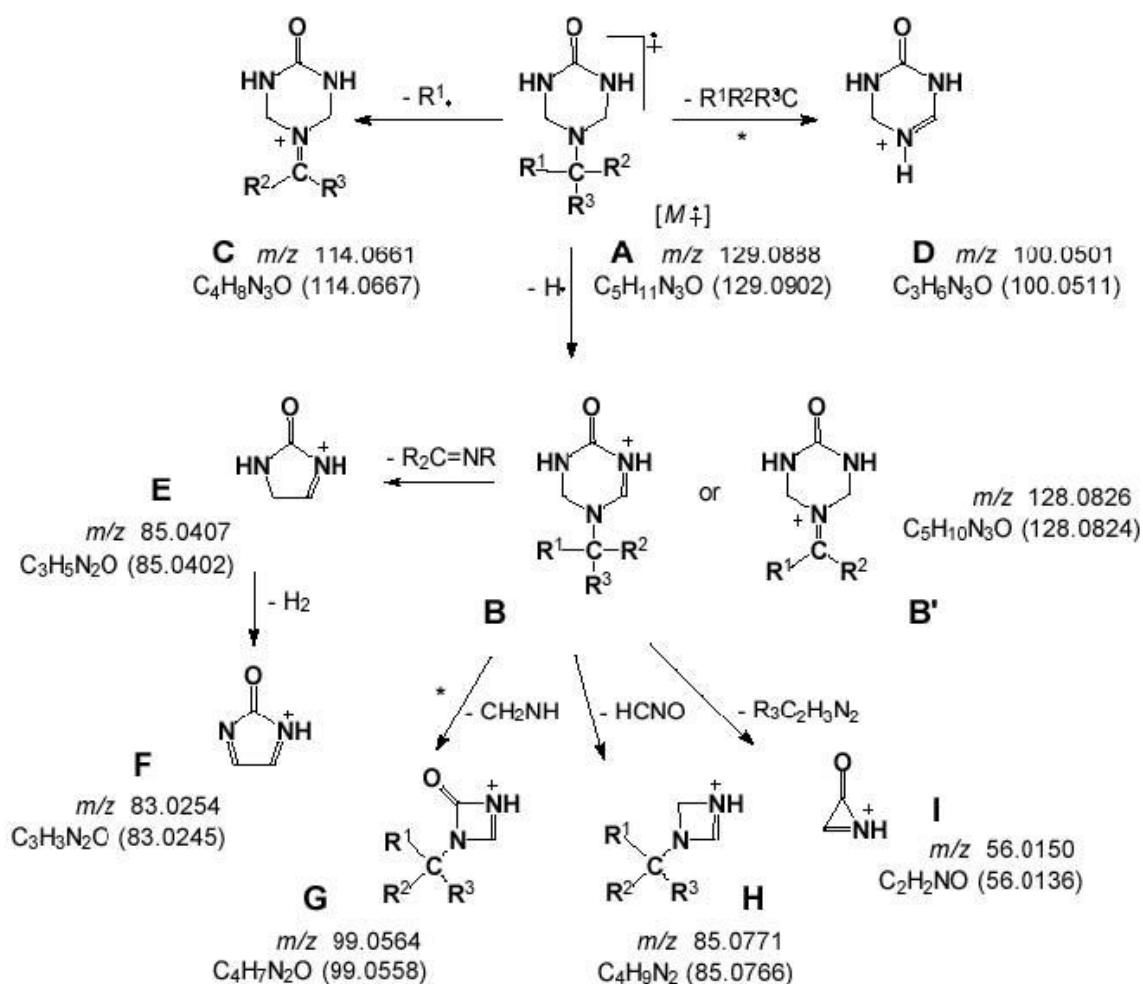
In all cases, loss of a hydrogen atom or an alkyl radical (R¹\$) from the 5-substituent of the molecular ion **A** would account for the corresponding even-electron species **B'** and **C** (Scheme 2).



Scheme 1

However, loss of a *ring* hydrogen would afford fragments of type **B**, in which delocalisation may be extended by involvement of the N(5) lone pair; consequently, ions of structural type **B** are considered more likely than the isomeric systems **B'**. Loss of the 5-substituent itself leads to the formation of cation **D** (m/z 100), which is common to all of the compounds examined; there is, in fact, metastable peak evidence for the direct formation of cation **D** from *both* the molecular ion **A** and the M-1 fragment **B**.

In addition to the foregoing fragmentations, in which the triazine nucleus remains intact, the 5-substituted 1,3,5-triazin-2-ones **3-8** appear to exhibit a series of extrusion/ring-contraction processes, resulting in the formation of 3- and 4-membered ring fragments. The resonance-stabilised cations **B** are considered pivotal in the formation of these heterocyclic fragments (**E-I**). Thus, elimination of a neutral imine ($R_2C=NR$) from the cation **B** would afford, in each case, the common, diazolinium ion **E** (m/z 85) (see Figure 1a), dehydrogenation of which gives cation **F** (m/z 83). On the other hand, extrusion of the neutral molecules, $CH_2=NH$ or $HN=C=O$, from cations of type **B** would afford fragments which retain the 5-alkyl substituent and which have been tentatively formulated as the diazetinones **G** and their deoxo analogues **H**, respectively. Access to these latter ions (**G** and **H**) is attributed to the similar, but fragment-specific eliminations depicted in Figures 1b and 1c; while there is metastable peak support for the fragmentation, **BG**, there is similar evidence, in some cases, for the loss of CH_3NH_2 from the molecular ion, *i.e.* **AG**. Elimination of a moiety containing the 5-substituent (Figure 1d) would account for the common cation at m/z 56, tentatively formulated as the azirininium species **I**.

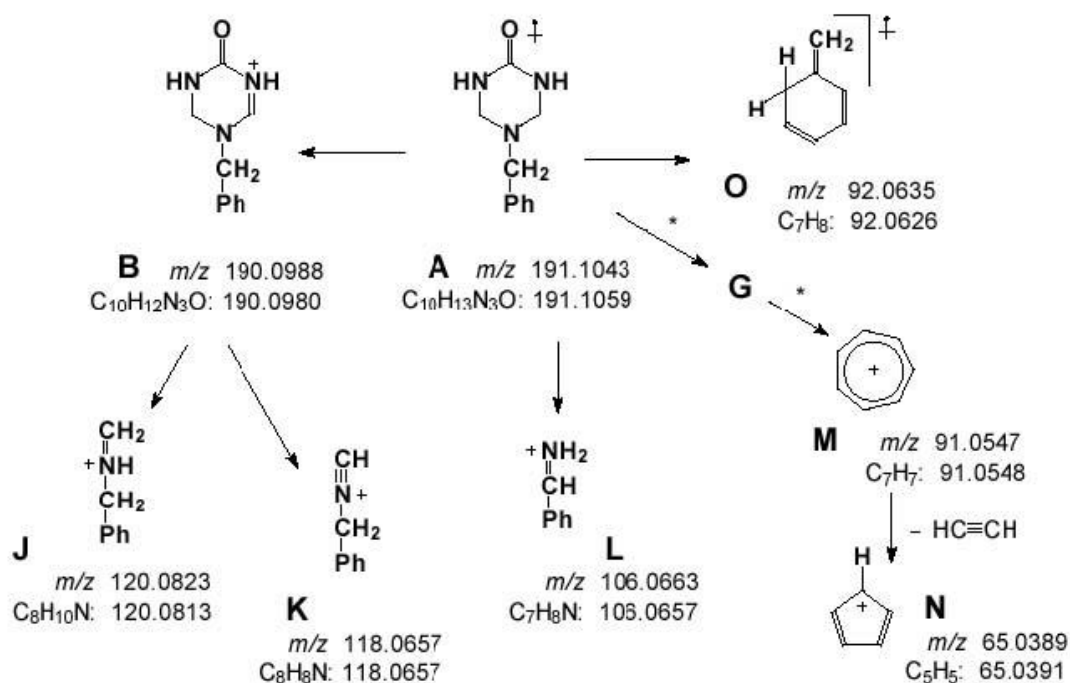


Scheme 2

Mass-spectral fragmentation pathways for the 1,3,5-triazin-2-ones **3** - **8**. Accurate masses (m/z) are followed, in parentheses, by calculated formula masses for compound **3** ($R^1 = \text{Me}$, $R^2 = R^3 = \text{H}$); an asterisk indicates a pathway supported by metastable peak data.

Accurate masses (m/z) are followed, in parentheses, by calculated formula masses; an asterisk indicates a pathway supported by metastable peak data.

The 5-benzyl derivative **8**, not surprisingly, exhibits a number of additional, characteristic fragmentations, all of which are supported by high-resolution data (Scheme 3). The base peak, in this case, corresponds to the tropylium cation **M** (m/z 91), metastable peak data supporting its formation *via* the sequence, **AGM**.



Scheme 3

Additional mass-spectral fragmentation pathways for 5-benzyl-1,3,5-triazin-2-one **8**.

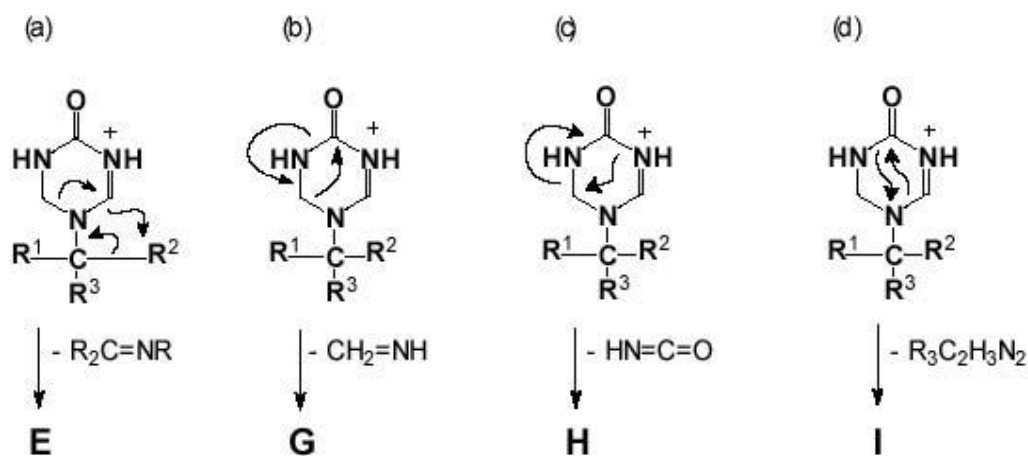


Figure1. Proposed fragmentations of the cations of type **B** to account for the formation of the heterocyclic fragments, **E**, **G**, **H** and **I**.

Experimental Section

General Procedures. NMR spectra were recorded in CDCl_3 on a Bruker AMX 400 NMR spectrometer and referenced using the solvent signals (δ_{H} 7.25 and δ_{C} 77.0 ppm). Low-resolution mass spectra were obtained on Hewlett-Packard 5988A and Finnigan Mat GCQ mass spectrometers. High-resolution EI data were collected on a VG-70SEQ mass spectrometer equipped with an MSS MASPEC II/32 data station (Cape Technikon Mass Spectrometry Unit), using high-resolution magnetic scans and B/E metastable scanning. Dimethylourea **1** [m.p. 129-130 °C (lit.⁷ 126-129 °C)] was prepared following a reported method.⁷ The synthesis of the 1,3,5-triazone derivatives, of which compounds **3**⁸ and **7** [158-159 °C (lit.⁶ 158 °C)] are known, is illustrated by the following example.

5-(2-hydroxyethyl)hexahydro-1,3,5-triazin-2-one (7). 2-Aminoethanol (2.5 ml, 0.042 mol) was added, with cooling, to dimethylourea **1** (5.0 g, 0.042 mol) in water (7 ml). The resulting solution was heated at 90-100 °C for two hours and then kept at room temperature overnight. The reaction mixture was concentrated under reduced pressure, and the solid residue recrystallised twice from ethanol to afford 5-(2-hydroxyethyl)hexahydro-1,3,5-triazin-2-one **7** (2.9 g, 47 %), (Found: M^+ 145.0853. Calc. for $\text{C}_5\text{H}_{11}\text{N}_3\text{O}_2$: M , 145.0851); ν_{max} ($\text{KBr}/\text{cm}^{-1}$) 3320 (OH), 3220 (NH) and 1660 (CO); δ_{H} (400 MHz; $\text{DMSO}-d_6$) 2.65 (2H, t, 1'- CH_2), 3.50 (2H, m, 2'- CH_2), 3.99 (4H, s, 2x CH_2), 4.51 (1H, br s, OH) and 6.27 (2H, br s, NH); δ_{C} (100 MHz; $\text{DMSO}-d_6$) 52.1 (1'- CH_2), 59.7 (2'- CH_2), 61.6 (2 x CH_2) and 154.7 (CO); m/z 145 (M^+ , 3.6 %) and 114 (100).

Analytical data for the new 1,3,5-triazinone derivatives prepared in this study are as follows.

5-Ethylhexahydro-1,3,5-triazin-2-one (3).⁸ (2.0 g, 19 %), m.p. 156-158 °C. (Found: M^+ 129.0910. $\text{C}_5\text{H}_{11}\text{N}_3\text{O}$ requires: M , 129.0902); ν_{max} ($\text{KBr}/\text{cm}^{-1}$) 3220 (NH) and 1650 (CO); δ_{H} (400 MHz; $\text{DMSO}-d_6$) 1.03 (3H, t, CH_3), 2.61 (2H, q, 1'- CH_2), 3.99 (4H, d, 2x CH_2) and 6.15 (2H, br s, NH); δ_{C} (100 MHz; $\text{DMSO}-d_6$) 13.0 (CH_3), 43.1 (1'- CH_2), 60.4 (2x CH_2) and 154.8 (CO); m/z 129 (M^+ , 30.2 %) and 128 (100).

5-Isopropylhexahydro-1,3,5-triazin-2-one (4). (1.9 g, 51 %), m.p. 179-180 °C. (Found: M^+ 143.1064. $\text{C}_6\text{H}_{13}\text{N}_3\text{O}$ requires: M , 143.1058); ν_{max} (hexachlorobutadiene mull / cm^{-1}) 3226 (NH) and 1673 (CO); δ_{H} (400 MHz; $\text{DMSO}-d_6$) 1.05 (6H, d, 2x CH_3), 2.93 (1H, septet, CH), 4.06 (4H, d, 2x CH_2) and 6.18 (2H, br s, NH); δ_{C} (100 MHz; $\text{DMSO}-d_6$) 21.0 (2x CH_3), 45.9 (CH), 58.5 (2x CH_2) and 155.0 (CO); m/z 143 (M^+ , 13.0%) and 128 (100).

5-*t*-Butylhexahydro-1,3,5-triazin-2-one (5). (2.7 g, 41 %), m.p. 181-182 °C. (Found: M^+

157.1209. $C_7H_{15}N_3O$ requires: M , 157.1215); ν_{\max} (KBr/ cm^{-1}) 3220 (NH) and 1690 (CO); δ_H (400 MHz; DMSO- d_6) 28.2 (3xCH₃), 52.9 [(CH₃)₃C], 56.7 (2xCH₂) and 155.4 (CO); m/z 157 (M^+ , 11.6 %) and 58 (100)

5-Butylhexahydro-1,3,5-triazin-2-one (6). (1.5 g, 23 %), m.p.128-130 °C (Found: M^+ 157.1218. $C_7H_{15}N_3O$ requires: M , 157.1215); ν_{\max} (hexachlorobutadiene mull / cm^{-1}) 3223 (NH) and 1666 (CO); δ_H (400 MHz; DMSO- d_6) 0.88 (3H, t, CH₃), 1.32 (2H, m, CH₃CH₂), 1.40 (2H, m, NCH₂CH₂), 2.55 (2H, t, NCH₂CH₂), 3.97 (4H, d, 2xCH₂) and 6.25 (2H, br s, NH); δ_C (100 MHz; DMSO- d_6) 13.7 (CH₃), 19.8, 29.5 and 48.8 ([CH₂]₃), 60.8 (2xCH₂) and 154.7 (CO); m/z 157 (M^+ , 27.5 %) and 42 (100).

5-Benzylhexahydro-1,3,5-triazin-2-one (8). (0.4 g, 5 %), m.p.190-192 °C. (Found: M^+ 191.1050. $C_{10}H_{13}N_3O$ requires: M , 191.1058); ν_{\max} (hexachlorobutadiene mull / cm^{-1}) 3062 (NH) and 1681 (CO); δ_H (400 MHz; DMSO- d_6) 3.78 (2H, s, CH₂Ph), 3.99 (4H, d, 2xCH₂), 6.35 (2H, br s, NH), 7.25 - 7.34 (5H, ArH); δ_C (100 MHz; DMSO- d_6) 53.3 (CH₂Ph), 60.5 (2xCH₂), 127.1, 128.2, 128.7 and 138.2 (ArC) and 154.6 (CO); m/z 191 (M^+ , 0.9%) and 91 (100).

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